Polysulfide speciation and reactivity in chromate-contaminated soil

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HIGHLIGHTS

- Calcium polysulfide reduced Cr(VI) in soil except Cr(VI) bound in PbCrO₄ particles.
- 96.5% of injected sulfur remained in the soil column up to 50 pore volumes of flow.
- Sulfur was present as elemental sulfur and thiosulfate in the treated soil.
- Up to 20% of thiosulfate was retained as PbS₂O₃ in the treated soil.

INTRODUCTION

Chromium has been one of the top 20 contaminants on the Superfund Priority List of Hazardous Substances for the last 15 years. Treatment of toxic and hexavalent chromium (Cr(VI)) in soil and groundwater often relies on the reduction of mobile, anionic chromate (CrO₄²⁻) to non-toxic and immobile cationic trivalent chromium (Cr(III)), either chemically or biologically [1]. Calcium polysulfide (CPS) is a reductant that has been used in the field at several Cr-contaminated sites [2–4] and to treat chromite ore-processing residue (COPR) [5] and contaminated soil for prolonged time periods (>1 year) [6–8]. Field studies reported successful reduction at initial aqueous chromate concentrations ranging from 60 μg/L [9] to 200 mg/L [4]. COPR studies reported variable success with CPS reduction of solid-bound chromate. Specifically, Wazne et al. [7], Tinum et al. [8], and Chrysochoou et al. [6] reported that chromate in COPR and soil appeared to be completely reduced using alkaline digestion and colorimetric analysis, contrary to the findings of complementary X-ray absorption spectroscopy and diffraction analyses. However, the comparison of chemical and spectroscopic studies indicated that residual reductive capacity was presented both in CPS-treated COPR and contaminated soil for prolonged time periods (>1 year) [6,7]. This was not the case with COPR treatments based on sulfide, such as pyrite [10]. Thus, a difference in the reactivity and speciation of CPS compared to sulfide is required to explain the different behavior of these two reductants.

Recently, Chrysochoou and Ting [11] studied the kinetics of aqueous chromate reduction by CPS and the speciation of sulfur, with and without oxygen. Chromate reduction by CPS was observed...
to follow second-order kinetics and was significantly faster compared to sulfide that follows first-order kinetics. The influence of pH on oxidation kinetics was also observed to be different for sulfide and CPS, with sulfide showing a constant acceleration with decreasing pH, while CPS showed a maximum at pH 7 under aerobic conditions. This behavior was attributed to the preferred oxidation of CPS to form thiosulfate in the presence of oxygen, while sulfide forms sulfite and sulfate. Thiosulfate is produced according to the reaction [12]:

\[ \text{S}_2\text{O}_3^{2-} + \frac{3}{2} \text{O}_2 \rightarrow \text{S}_2\text{O}_4^{2-} + (x - 2)\text{S}^0 \]  

In contrast, the oxidation of sulfide through the reduction of chromate produces elemental sulfur according to the reaction:

\[ 2\text{CrO}_4^{2-} + 3\text{CaS}_2 + 10\text{H}^+ \leftrightarrow 2\text{Cr}^{3+}(\text{aq}) + 15\text{S}(\text{s}) + 3\text{Ca}^{2+} + 2\text{H}_2\text{O} \]  

This study further explores the reductive capability and speciation of sulfur in a CPS-treated, chromate-contaminated soil, utilizing spectroscopic techniques in combination with a traditional column study.

2. Materials and methods

2.1. Soil samples and characterization

Soil samples were obtained from a Cr-plating facility in Connecticut as described in Chrysochoou et al. [6]. Soil characteristics are shown in Table S1. Briefly, the soil is obtained from the surficial layer (top 5 ft) of an area adjacent to the facility that is highly contaminated with both Cr (11,900 mg/kg) and Pb (13,200 mg/kg). Approximately 40% of the Cr is present in the hexavalent form (5000 mg/kg). The Cr source is the discharge of plating bath solutions from the facility into the soil, while the source of Pb is unknown. Prior to the initiation of this investigation, the presence of Pb contamination in the soil was not suspected, but the very high concentrations point to anthropogenic contamination related to the facility activities. The two contaminants have been previously observed to be closely associated as PbCrO₄ [6]. The stoichiometry between the two elements indicates that 63.8 mmol/kg of Pb can be completely bound by the 96 mmol/kg Cr(VI) present in the sample. Other co-contaminants are Ni, which is present at a higher than background concentrations (440 mg/kg). The soil is a glacial till with relatively high Fe content (32,000 mg/kg), which consists primarily of quartz and aluminosilicates such as feldspar and mica [6].

2.2. Column studies

Four columns were set up for this study, two control (denoted as CTRL-1 and CTRL-2) and two treated with approximately 0.5 pore volume (PV) (25 mL) of 29% CaS₂ solution (denoted as CPS-1 and CPS-2), which corresponded to 1× stoichiometric ratio for the chromate mass in the column. The column set up was identical to the column tests described in Chrysochoou et al. [13], and the description is also provided in the Supplementary Information. All columns were operated at 0.1 mL/min injected from the bottom of the column; this flow rate corresponds to the upper limit of groundwater flow observed at the site [13]. The entire system was closed to the atmosphere by purging both the influent and the effluent bottles with nitrogen. A leaching solution that simulated groundwater at the site was used for all columns as described in Chrysochoou et al. [13] and Table S2. The CPS solution was injected into the treated columns at PV 6 and all columns were monitored for a total of 50 PVs. The effluents from the columns were regularly analyzed for pH, redox potential, and Cr(VI) and total Cr concentrations. Selected measurements were taken for total S, Fe, Mn, Ni, and Pb concentrations. Upon termination, the columns were disassembled and characterized in three layers for total metals, total Cr(VI), pH, and redox potential. All analytical methods are presented in the Supplementary Information.

2.3. Bulk XANES

A separate batch study was set up to conduct bulk XANES analyses using the same soil sampled for the column studies. Thirty grams of soil was mixed with 3, 6, 12, and 24 mL of 29% CPS solution (1×, 2×, 4×, and 8× stoichiometric ratios, respectively), and nitrogen-purged deionized water was added to achieve a total volume of 30 mL. The samples were mixed, purged with nitrogen, and sealed for 1 month prior to XANES analysis. The 2× stoichiometry was also tested at 0 days, 7 days, 2 months, and 3 months of curing time. Control samples without CPS were prepared at 1- and 90-day time intervals. Triplicate samples were prepared for all dosages and curing times. XANES data were obtained at the Cr K-edge (5989 eV) and S K-edge (2472 eV) on beamline 4-3 at the Stanford Synchrotron Radiation Lightsource at the SLAC National Accelerator Laboratory; details are provided in Supplementary Information.

2.4. Micro-X-ray analyses

Two samples from the middle sections of the CTRL-1 and CPS-1 columns were prepared as 30 μm diamond-polished thin sections by Spectrum Petrographics (Vancouver, WA). Micro-XRF, μXRD, and μXANES measurements were performed on beamline 10.3.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Micro-XRF elemental maps were acquired at 13.5 and 3.9 keV incident energies with a beam size of 10 μm × 10 μm and a counting time of 120 ms/pixel. Fluorescence counts were collected for Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, and Pb in the 13.5 keV map and S in the 3.9 keV map with a seven-element Ge solid-state detector. Chromium mapping was performed at incident energies of 5980, 5993, and 6250 eV to obtain the background, Cr(VI), and total Cr signals, respectively. Energy calibration was performed using a Cr foil (5989 eV). The three maps were used to obtain maps for the Cr(VI) and Cr(III) signals using the chemical mapping analysis method described by Marcus [14] and employing PbCrO₄ and Cr(OH)₃ as XANES standards. Various spots of interest were selected for Cr K-edge μXANES and μXRD to probe Cr speciation. In addition, XANES was performed on selected spots of a batch sample treated with 2× CPS for 2 months (details are discussed in [6]). Energy calibration for S was performed using Na₂S₂O₃.

3. Results and discussion

3.1. Column studies

Fig. 1 shows the pH, redox potential, chromate (as Cr(VI)), and total S in the column outflow. Under the conditions of the study, hexavalent chromium is either present as chromate (CrO₄²⁻) or HCrO₄⁻ below the pKₐ of 6.5; for the remainder of the discussion, these species will be collectively referred to as Cr(VI). Fig. S1 shows the concentrations of total Cr, Pb, Fe, Ni, and Mn. The control columns maintained a pH of 5.5 and an Eh of 200 mV throughout the monitoring period. The Cr(VI) concentration ranged from 0.3 to 0.45 mg/L during the first 6 PVs, presumably due to initial flushing of exchangeable chromate; after PV 6 the Cr(VI) concentration remained constant at approximately 0.16 mg/L, indicating solubility control. Chrysochoou et al. [6] reported that PbCrO₄ was the primary sink for chromate in this soil, which was also confirmed by the bulk and micro-XANES analyses. Modeling of a Pb-Cr(VI) aqueous solution indicated that the solubility of Cr(VI) with
respect to PbCrO$_4$ at pH 5.5 and Pb concentration of 0.3–0.5 mg/L is 0.05–0.13 mg/L, which is quite close to the measured concentration. In the treated column, the Cr(VI) concentration decreased to non-detectable values (<0.025 mg/L) upon injection of CPS and remained below the detection limit for the remainder of the experiment (PV 50). The redox potential (Fig. 1b) initially decreased to −500 mV at PV 6, but increased to positive values by PV 10 and progressively returned to the control value of 200 mV. Similarly, the pH was initially influenced by the injection of alkaline CPS solution (pH 11.5), but progressively returned to near-neutral conditions by PV 50.

Sulfur leaching was very high immediately following injection, reaching 3660 mg/L at PV 6. It decreased to 70 mg/L by PV 12, 20 mg/L by PV 20, and reached background values by the end of the experiment. The effluent was also monitored using a sulfide-specific probe, which indicated that sulfide was present only during the initial PV following injection; by PV 10, it was below the detection limit (0.003 mg/L). Although the exact speciation of sulfur in the effluent was not determined, possibilities include thiosulfate ($S_2O_3^{2−}$), sulfite ($SO_3^{2−}$), and sulfate ($SO_4^{2−}$). Thiiosulfate has been found to form preferentially as a result of CPS oxidation [11,15]. Despite the high concentration of sulfur in the outflow, the overall amount leached (~210 mg) was very small compared to the amount added (3800 mg), which corresponds to 96.5% of sulfur retained in the soil.

The strongly reducing environment and elevated pH conditions created by CPS resulted in mobilization of metals, including Cr(III), Pb, and Ni (Fig. S1). The dissolved metal front was quickly attenuated as the redox potential returned to positive values at PV 10. No substantial mobilization of Fe or Mn was observed at any time point (Fig. S1).

The post-mortem analyses of the column soil yielded non-detectable values of Cr(VI) in the solid using the conventional EPA methods 3060A and 7196. This method has been previously to be unreliable in CPS-treated solids [6], thus bulk and micro-XANES analyses were employed instead to assess the true extent of chromate reduction in the solid phase, as well as speciation of sulfur.

Fig. 2 shows the percentage of Cr(VI) in the solid determined by bulk XANES and µXRF at 2× dosage as a function of curing time (a) and at 30 days curing time as a function of dosage (b).

### 3.2. Bulk XANES

Fig. 2 shows the percentage of Cr(VI) in the solid determined by bulk XANES as a function of time and CPS dosage. The majority of reduction at 2× stoichiometry occurred during the first 30 days of curing, with Cr(VI) decreasing from an average of 30 to 17% ($p < 0.001$); this corresponds to absolute Cr(VI) concentrations of 4000 and 2040 mg/kg for an average total Cr concentration of 12,000 mg/kg (Table 1). These results are in good agreement with µXANES results reported by Chrysochoou et al. [6] for 60-day cured batch samples. No statistically significant differences ($p_{1M−2M} = 0.57$, $p_{2M−3M} = 0.2$) were observed between subsequent data points, so that Cr(VI) reduction substantially slowed down or altogether stopped at 30 days. The redox potential remained, however, at −500 mV in all samples up to 90 days, given that they were closed to the atmosphere, and the pH was constant at 11. When the stoichiometry of added CPS was increased from 2× to 8× at 30 days curing time, the Cr(VI) percentage decreased to 11% ($p_{2X−8X} = 0.007$), while the intermediate dosage of 4× did not
yield a statistically significant difference in the Cr(VI) percentage (pX,0.4 = 0.83). Similarly, the redox potential was at −500 mV and the pH at 11 for all samples tested.

The S XANES spectra of the cured samples and reference compounds are shown in Fig. 3, and the primary peak positions of the different oxidation states are summarized in Table 1. The reference compounds had similar features and peak positions to standard spectra reported elsewhere [16,17]. The spectrum of pure calcium polysulfide showed peaks at 2471.6 and 2473.4 eV, which correspond to the absorption energies of sulfide and elemental sulfur, respectively. Similar results were reported by Vairavanurthy [17], who assigned the 2473.3 eV peak to di- and polysulfidic sulfur. The oxidation states of the polysulfide ions are −2 at the end and 0 in the middle of the chain [18], so that the peak positions and formal oxidation states are in agreement. Two additional peaks were observed at 2479.8 and 2481.4 eV, which are similar to secondary peak positions of thiosulfate (2480 and 2481.6 eV). It is plausible that some thiosulfate is formed in the polysulfide solution upon exposure to the atmosphere. One difference that could distinguish the two compounds is that the height ratio of the two peaks in the CPS spectrum is 1.005, while the respective ratio in the Na2S2O3 spectrum is 1.23; this is likely because the zero oxidation state in the CPS chain contributes intensity to the 2480 eV, but not to the 2481.6 peak.

The spectra of the cured samples all had quite similar features. Attempts to fit the experimental spectra by linear combination of the standard compounds yielded poor results because of self-absorption effects and because the physical state of the sulfur species in the samples was not identical to the standard spectra, which is required for accurate quantitative analysis of S XANES spectra [19]. Thus, we used qualitative observations to draw conclusions about S transformation in the soil.

Peaks were observed for all samples at 2473.3, 2480.0, and 2481.4 eV, and a few spectra had a shoulder at 2471.6 eV. This peak that indicates the presence of sulfide species (either as sulfide or polysulfide) was identified in samples cured for 0 and 7 days at 2× CPS dosage and in samples cured for 1 month at 4× and 8× stoichiometry. Thus, residual reductive capacity in the form of sulfide was observed at short curing times or high dosages. In contrast, longer curing times (>1 M) and lower dosages (<2 ×) exhibited broadening of the 2473.3 eV peak, which is characteristic of the elemental sulfur spectrum (Fig. 2b). The peaks at 2480.0 and 2481.4 eV may be attributed to several species, including elemental S, polysulfide, thiosulfate, and galena. Galena has a characteristic peak at 2477.9 eV that was not identified in any of the sample spectra and was thus excluded from further consideration. Polysulfides are only stable in solution at alkaline pH, since their pKa values are at 9.2 or higher [20]. The pH of the batch samples was maintained above 10 up to 1 month of curing and above 9 up to 3 months of curing at 2× stoichiometry, so that the presence of polysulfides is not implausible in any of the samples with peaks at 2471.6 eV. In the remaining samples, the spectrum appears to be a combination of elemental sulfur and thiosulfate. A broader peak at 2473.3 eV indicates a higher amount of elemental sulfur, while a more pronounced peak at 2481.4 eV indicates a higher concentration of thiosulfate. Using this criterion, it appears that the 1M–1X sample had a higher thiosulfate concentration, while 1M–2X had some thiosulfate but more elemental sulfur, and higher dosages had residual sulfide/polysulfide that dominated the spectra. The spectra obtained at 2× dosage up to 3 months of curing showed that thiosulfate was present up to 90 days, with the sulfur peak at 2480.0 being slightly more pronounced at 90 days, indicating that additional reactions occurred, albeit at a slow pace.

### 3.3. Micro-X-ray analyses

Three μXRF maps were acquired for the column samples, with a total area of 7.1 mm² in the untreated sample and 8.8 mm² in the treated sample. The tricolor Cr(VI)–Si–Fe maps are shown in Fig. S2, and the Cr(VI)PbS maps for the column and batch samples are shown in Fig. 4.

Cr(VI) was primarily present as small grains in the interstitial spaces between larger quartz and feldspar grains and associated with Pb. The bulk measurements of the two compounds indicate that up to 66% of Cr(VI) may be bound as PbCrO4. The correlation coefficient between the counts of the two elements was 0.57, which provides an excellent agreement between the two measurements. Cr(VI) association with Fe was observed in a few grains in the untreated sample (Fig. S2). While the overall correlation coefficient between Fe and Cr(VI) counts was very low for the entire area (R² = 0.08), it was 0.94 when these grains were isolated. This indicates that some of the Cr(VI) was sorbed on Fe oxide coatings, a mechanism that is plausible at pH 5.5 of the untreated soil. The correlation coefficient for Pb and Cr(VI) counts increased from 0.57 in the untreated areas to 0.92 in the treated area, indicating that Cr(VI) that was not present as PbCrO4 was preferentially reduced upon CPS addition. This is corroborated by the fact that areas with low Cr(VI) counts were preferentially eliminated in the treated sample. The bulk measurements indicate that approximately one-third of the initial Cr(VI) was not bound by Pb and more available for reduction. The batch XANES analyses further showed that this more available Cr(VI) fraction was reduced by 30 days curing and that the remaining fraction that was almost exclusively present as PbCrO4 was recalcitrant to treatment, despite the persistence of highly reducing environment (−500 mV).

The μXRF maps (Fig. 4c and d) show that sulfur was present in two main forms: concentrated in bright green spots and diffuse within the matrix, where it was associated with other elements, particularly Pb and Cr. Given that Pb presented high correlation with Cr(VI) in the treated maps, we isolated the areas with high S–Cr and S–Pb correlations, the tricolor maps of which are shown in Fig. 5. Six points were selected in these areas (Fig. 5) and subjected to μXANES analysis, the spectra of which are shown in Fig. 3d.

Points P0 and P1 were mostly green (Fig. 5a and b), which corresponds to S in the tricolor maps, and the respective μXANES spectra closely matched elemental sulfur. Thus, it is concluded that the bright green areas in Fig. 4d correspond to pure elemental sulfur, produced by the reaction of (poly)sulfide and chromate, as predicted by redox reaction 1.

Fig. 5a indicates that even when Pb was in close proximity, there was limited tendency for sulfide to be scavenged and form galena (PbS), but remained as free Pb (more likely Pb carbonate or oxide) after chromate was released from PbCrO4, which was observed to bind practically all available Pb in the untreated sample (Fig. 4a and b). The area around P2 was similar, and the μXANES spectrum was quite close to elemental sulfur, but it clearly included another species, most likely thiosulfate. Points P3 and P4 show even more prominent features similar to thiosulfate in the region around 2480 eV. The μXRF map indicates that the corresponding points consist primarily of S (green) with some Pb (blue) as well.

### Table 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Oxidation state</th>
<th>Main peak (eV)</th>
<th>Additional peaks (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS2</td>
<td>−2</td>
<td>2471.5</td>
<td></td>
</tr>
<tr>
<td>PbS4</td>
<td>−2</td>
<td>2472.7</td>
<td>2482.0</td>
</tr>
<tr>
<td>CPS</td>
<td>−2, 0</td>
<td>2471.6, 2473.4</td>
<td>2479.8, 2481.4</td>
</tr>
<tr>
<td>S8</td>
<td>0</td>
<td>2473.2</td>
<td></td>
</tr>
<tr>
<td>Na2S2O3</td>
<td>−2, +6</td>
<td>2472.6</td>
<td>2480.0, 2481.6</td>
</tr>
<tr>
<td>Na2SO3</td>
<td>+4</td>
<td>2479.0</td>
<td>2481.0, 2482.6</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>+6</td>
<td>2483.4</td>
<td></td>
</tr>
</tbody>
</table>

*Summary obtained from ESRF ID21 sulfur XANES database [33].*
The area with the most prominent association of Pb and S was the grain around P6 (Fig. 5f). The μXANES spectrum indicated that S was present primarily as thiosulfate, which forms PbS₂O₃ with a solubility of 300 mg/L at 15 °C H₂O [21]. While the solubility of this compound is relatively high, the high sulfur concentrations in the column effluents (Fig. 1d) and the high ability of S to remain in the solid may be conducive to its stability, especially at short time frames. Its continuous dissolution in water may in fact be favorable towards additional reduction of slowly released chromate. Fig. 5e supports this notion, given that μXANES shows a clear thiosulfate spectrum, while the μXRF map indicates the co-existence of all three elements, with Cr(VI) contributing the majority of the

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**Fig. 3.** S K-edge XANES spectra of (a) batch samples cured with 2 × CPS, (b) standard compounds (galena reference obtained from [33]), (c) batch samples cured with various dosages at 1 month curing time, and (d) micro-XRF sample treated with 2 × CPS for 2 months.

**Fig. 4.** Tricolor μXRF maps of untreated column sample (a and b), treated column sample (c), 60-day cured batch sample (d), and detail of rectangular insert in treated column sample (e). All intensities scaled to constant Fe content. The same spatial scale was used in all figures except (e).
observed counts (as indicated by the pink color). A large grain with high Pb–S correlation was also observed in the column sample (Fig. 4e), however no XANES spectrum is available for that area.

The column contained approximately 3300 mg of Pb (13,200 mg/kg in 250 g soil) or approximately 16 mmol, which could bind up to 32 mmol or 1024 mg of S as PbS2O3. This is approximately 20% of the total S that was retained in the soil column (5600 mg). Thiosulfate does not form any other insoluble precipitates in soil environments, so that the only other known retention mechanism is sorption to iron oxides, which are positively charged at pH<8–9 [22]. Even though no crystalline iron oxides were identified in the soil matrix by XRD, the high Fe concentration in the soil indicates that amorphous Fe oxyhydroxides are most likely present. Given that polysulfides create an alkaline environment, a sorption mechanism is likely not favored for anionic thiosulfate at short curing times; however, as the pH decreased below 8 after 20 PV in the column experiments, sorption may enhance thiosulfate retention in the soil.

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Fig. 5. µXRF tricolor maps of areas with high S–Cr and high S–Pb correlation in batch–sample marked points corresponding to XANES spectra in Fig. 3d.
3.4. Implications for treatment

The XANES and micro-XANES results clearly indicated that there are two main sulfur species that are present in CPS-treated soil long-term (days and months after treatment): elemental sulfur, which is the main oxidation product by reaction with chromate, and thiosulfate. Both were present under strongly reductive conditions (−500 mV) in the absence of oxygen. While thiosulfate is a reductant for Cr(VI), it requires strongly acidic conditions for effective reduction; above pH 2.5, the kinetic rate of reduction becomes almost zero [23]. IETEG [2] reported no Cr(VI) reduction by Na2S2O3 at neutral pH conditions and 3 h of reaction time. Thus, it is considered unlikely that direct reduction of chromate by thiosulfate is a viable long-term reductive mechanism in CPS-treated soil.

The production of naturally occurring Fe(II) in soils treated with CPS and sodium dithionite has been previously reported [24,25]. The mobilization of iron in the column outflow in the initial phases after CPS injection (Fig. S1) is indicative of reduction of Fe bound in Fe(III)-oxides in the soils, however the long-term fate of Fe in the column is unknown. The presence of thiosulfate can aid the persistence of Fe(II) that remains sorbed on iron oxides at the alkaline pH of the soil via two mechanisms: direct reduction of Fe(III), or scavenging of oxidants, including any dissolved oxygen. Su and Ludwig [26] observed retardation in the rate of Fe(II) oxidation in the presence of dithionite and attributed this phenomenon to oxygen scavenging by dithionite and sulfite, both of which are used in the petroleum industry to strip oxygen from water [27,28]. Thiosulfate has been shown to react with Fe(III)-bearing phyllosilicates to produce Fe(II) and S2O42−, even though it is a less potent reductant compared to sulfide and dithionite [29]. In acidic conditions, thiosulfate decomposes to sulfite and elemental sulfur, while it is stable in neutral environments [30]. Thiosulfate will react with oxygen only in the presence of a mineral catalyst, such as pyrite (FeS2) and sphalerite (ZnS) doped with transition metals [31,32]. Given the apparent absence of sulfidic minerals, oxygen scavenging is likely not an important mechanism; persistence of Fe(II) viable mechanism to sustain long-term reductive environment. If this conclusion holds, the presence of iron in the system can enhance CPS performance. Additional studies on the fate of iron in the system are required to investigate this hypothesis.

4. Conclusions

Treatment of Cr(VI)-contaminated soil with a stoichiometric dosage of CPS indicated that the majority of sulfur (96.5%) was retained within the soil column for 45 PV, which corresponded to approximately 3.5 months of groundwater flow at the site, with a velocity of 0.03 m/day. Sulfide and low redox potential were short lived in the column effluent, with the redox potential increasing from −460 to +130 mV after 3 PV of simulated groundwater flow. Chromium(VI) was not detected in the column effluent at any time point after CPS injection, even though it was established from previous studies that it is mostly bound in the soil as PbCrO4 and thus leaches slowly from the solid matrix into solution.

Bulk and micro-XANES analyses confirmed that Cr(VI) that was not present as PbCrO4 was completely reduced, while PbCrO4 was recalcitrant to treatment, despite the persistence of a reducing environment as indicated by the redox potential. The soil maintained a reducing capacity even after sulfide was no longer detected in solution. Both bulk and micro-XANES analyses indicated that sulfur speciation in both the batch and column solids was a combination of elemental sulfur and thiosulfate. The micro-XRF analyses indicated that elemental sulfur precipitated as larger discrete particles, while thiosulfate was observed to be diffuse within the soil grains, associated in some cases with Pb. It is concluded that PbS2O3 may have bound up to 20% of sulfur within the soil column. Sorption of thiosulfate to abundant iron oxides present is also a likely retention mechanism in the soil below pH 8. Given that thiosulfate cannot reduce chromate but can reduce Fe(III) even when bound in minerals under neutral pH conditions, it is hypothesized that long-term reduction of Cr(VI) in CPS-treated soil may be enhanced by the presence of Fe oxides.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2014.07.022.

References